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(54) [Title of the Invention] High-Strength, High-Conductivity Copper Alloy for Electronic Equipment Having Excellent Bendability and Stress Relaxation Properties

(57) [Abstract]

[Problem] To provide a high-strength, high-conductivity copper alloy for inexpensive electronic devices having excellent strength, electrical conductivity, bendability, stress relaxation properties, solderability, and other properties.

[Means for Solving Problem] A high-strength, high-conductivity copper alloy for electronic devices comprises 0.01 to 4.0% Ti, 0.05 to 0.8% Cr, 0.05 to 0.4% Zr, and 0.005% or more but less than 0.05% Mg, or further contains one or more elements selected from 0.05 to 2.0% Zn and one or more of the following elements: Sn, In, Mn, P, Ni, Si and Fe in an amount totaling 0.01 to 1.0%, with the remainder consisting of Cu and unavoidable impurities, and the average crystal grain size is adjusted to 35 to 100 μ m.

[Claims]

[Claim 1] A high-strength, high-conductivity copper alloy for electronic devices having excellent bendability and stress relaxation properties, characterized in that it comprises by weight ratio, 0.01 to 4.0% Ti, 0.05 to 0.8% Cr, 0.05 to 0.4% Zr, and 0.005% or more but less than 0.05% Mg, with the remainder consisting of Cu and unavoidable impurities, and the average crystal grain size is adjusted to 35 to 100 μm. [Claim 2] A high-strength, high-conductivity copper alloy for electronic devices having excellent bendability and stress relaxation properties, characterized in that it comprises by weight ratio, 0.01 to 4.0% Ti, 0.05 to 0.8% Cr, 0.05 to 0.4% Zr, 0.005% or more but less than 0.05% Mg, and 0.05 to 2.0% Zn, with the remainder consisting of Cu and unavoidable impurities, and the average crystal grain size is adjusted to 35 to 100 µm. [Claim 3] A high-strength, high-conductivity copper alloy for electronic devices having excellent bendability and stress relaxation properties, characterized in that it comprises by weight ratio, 0.01 to 4.0% Ti, 0.05 to 0.8% Cr, 0.05 to 0.4% Zr, and 0.005% or more but less than 0.05% Mg and further contains one or more elements selected from Sn, In, Mn, P and Si in an amount totaling 0.01 to 1.0%, with the remainder consisting of Cu and unavoidable impurities, and the average crystal grain size is adjusted to 35 to 100 μm. [Claim 4] A high-strength, high-conductivity copper alloy for electronic devices having excellent bendability and stress relaxation properties, characterized in that it comprises by weight ratio, 0.01 to 4.0% Ti, 0.05 to 0.8% Cr, 0.05 to 0.4% Zr, 0.005% or more but less than 0.05% Mg, and 0.05 to 2.0% Zn, and further contains one or more of the following elements selected from Sn, In, Mn, P and Si in an amount totaling 0.01 to 1.0%, with the

remainder consisting of Cu and unavoidable impurities, and the average crystal grain size is adjusted to 35 to $100 \ \mu m$.

[Detailed Description of Invention]

[0001]

[Industrial Field of Use] The present invention relates to a copper alloy for electronic devices that is ideal for the lead frame material in a semiconductor integrated circuit (IC), and the conductive spring material in various terminals, connector relays, switches, and the like.

[0002]

[Prior Art and Problems] Cobal (Fe-29Ni-16Co), 42 alloy (Fe-42Ni), and other high-nickel alloys have been the material of first choice for leads in semiconductor equipment because they have a low thermal expansion rate, exhibit good adhesion, and provide a good seal with semiconductor components and ceramics. However, "copper alloys" with good heat radiating performance are now also used as lead materials because many ICs now consume large amounts of electricity as a result of the improvement in the degree of integration of semiconductor circuits, and because adhesion between the components and lead frames has been improved with the increased use of resins as sealing materials.

[0003] However, lead materials of semiconductor equipment must generally have the following properties.

- a) The lead is the part that transmits electrical signals and at the same time plays a role in releasing to the outside the heat that is generated during the packaging step and during circuit use; therefore, it must have excellent conductivity of heat and electricity.
- b) The adhesion between the lead and the mold material is important in terms of "protecting the semiconductor components;" therefore, the lead material must have a coefficient of thermal expansion that is close to that of the mold material.
- c) The lead material must have good heat resistance because it is put through various heating steps during packaging.
- d) The lead material is virtually always subjected to punching and bending during lead production; therefore, the lead material must have good workability during such punching and bending.
- e) The lead material generally has a noble metal-plated surface when used as a lead; therefore, it must have good adhesion with this noble metal plating.
- f) The lead material is often soldered to the so-called "outer lead part" that remains outside of the sealing material even after packaging; therefore, the lead material must display good solderability and the solder must not peel with long-term use.
- g) The lead material must have good resistance to corrosion, which has a strong impact on the reliability and service life of the equipment.
 - h) The lead material should be inexpensive.

[0004] Nevertheless, alloys that have been used as the lead material of semiconductor devices all have advantages and disadvantages in terms of each of the above-mentioned requirements and an alloy that satisfies all of these requirements in good balance has yet to be discovered.

[0005] On the other hand, inexpensive "brass," "phosphor bronze" having excellent spring properties, and "nickel silver" having excellent spring properties and corrosion resistance have been used in spring materials, including terminals, connectors, relays, and switches. However, problems with product value have been unavoidable because brass has poor strength and bending properties; phosphor bronze, which has excellent bending properties, has a high Sn content, and nickel silver, which has excellent strength and bending properties, has a high Ni content, and the starting material cost of both is high; in addition, there are problems in that workability is limited because of deterioration with hot working; and the like. Furthermore, when being considered for use in electronic device parts that have strict property requirements, it cannot be said that any of these materials are satisfactory in terms of electrical conductivity. Also, in terms of connector properties, they pose a disadvantage in that "stress relaxation properties at contacting parts are poor."

[0006] In particular, the workability of the material has become even more important in recent years as electronic devices and the parts used in these devices have become smaller and thinner, and bendability (bending workability) in particular must be excellent. Therefore, there is a need for an alloy for electronic devices that is inexpensive, of course has excellent conductivity, but also has excellent spring properties and bendability.

[0007] "Cu-Ti alloys" and "Cu-Cr alloys" satisfy to a considerable extent the above-mentioned properties required of electronic device materials; therefore, several new alloys have been developed by adding a third and fourth element to the above-mentioned alloys in an attempt to improve properties.

[0008] However, today there has been accelerated progress in making highly integrated, high-precision semiconductor circuits, and this has led to lead frames that have many pins and are very thin. Therefore, the lead frame material must be even stronger than in the past. Moreover, for the first time, the connectors must be made of a material that rivals beryllium copper in strength in terms of improving reliability and releasing heat (improving strength is an efficient means for improving the release of heat even when the part is thin). Consequently, although several new copper alloys have been developed with a Cu-Ti or Cu-Cr base, the copper alloys developed thus far have not satisfied the above-mentioned requirements.

[0009] Therefore, the object of the present invention is to provide an inexpensive, high-conductivity copper alloy for electronic devices which, of course, has excellent electrical conductivity and a strength rivaling that of high-strength spring materials such that it can be used for multipin lead frames, and has the same or better stress relaxation properties, bendability, and other properties as conventional copper alloys for electronic devices.

[0010]

[Means for Solving Problems] As a result of performing intense research in order to accomplish the above-mentioned object, the inventors obtained the new knowledge that "a copper alloy comprising Ti, Cr, Zr, and Mg at a closely restricted predetermined ratio as the alloy components and having an average crystal grain size that has been adjusted to within a range of 35 to 100 µm, in particular, by selecting the conditions for solution annealing treatment, and the like has the strength, electrical conductivity, bendability, stress relaxation properties, and other properties, both on the

high level required for future electronic devices and in good balance, and a further improvement of solderability and strength is possible by adding Zn, Sn, In, Mn, P, and Si in appropriate amounts."

[0011] The present invention was completed based on this knowledge, and is primarily characterized in that "a high-strength, high-conductivity copper alloy for electronic devices

has high electrical conductivity, high strength, excellent bendability and stress relaxation properties, and good solderability

because it comprises 0.01 to 4.0% Ti (the % representing the component ratios indicate wt% here and below), 0.05 to 0.8% Cr, 0.05 to 0.4% Zr, and 0.005% or more but less than 0.05% Mg,

or further contains one or more elements selected from 0.05 to 2.0% Zn and one or more of the following elements: Sn, In, Mn, P, and Si in an amount totaling 0.01 to 1.0%, with the remainder consisting of Cu and unavoidable impurities, and because the average crystal grain size is adjusted to 35 to $100~\mu m$.

[0012] The reasons for limiting the components and crystal grain size of the alloy of the present invention as described above will now be described in detail together with the operation of the invention.

[Operation of the Invention]

A) Component ratios

Ti

The Ti acts to create a structure of irregular concentration in the base material by spinodal decomposition when the alloy is aged and as a result, guarantees a very high

strength. However, the desired effect of this action cannot be expected if the Ti content is less than 0.01%. On the other hand, if the Ti content exceeds 4.0%, reaction-type precipitation will tend to occur at the grain boundaries and this will lead to a reduction in strength and a reduction in workability. Therefore, the Ti content was set at 0.01 to 4.0%.

[0013] Cr

Cr acts to improve the strength and heat resistance of the alloy as a result of precipitating alone in the base material and precipitating as a compound of spinodal decomposition when an alloy is aged as with the above-mentioned Ti. The desired effect of this action cannot be expected if the Cr content is less than 0.05%, while if the Cr content exceeds 0.8%, Cr that is not in solid solution form will remain in the base material after solution annealing and there will be an obvious drop in electrical conductivity and workability.

[0014] <u>Zr</u>

Zr acts to form a compound with Cu, which precipitates in the base material, and strengthens the base material during aging. If the Zr content is less than 0.05%, the desired effect of this action will not be obtained, while if the Zr content exceeds 0.4%, Zr that is not a solid solution will remain in the base material after solution annealing and this will lead to an obvious reduction in electrical conductivity and workability.

[0015] Mg

Mg acts to considerably improve the stress relaxation properties, even when added in a trace amount. However, if the Mg content is less than 0.005%, the desired effect of this action cannot be expected, while when 0.05% or more is added, this effect

becomes saturated and there is a reduction in electrical conductivity. Therefore, the Mg content was set within a range of 0.005% or greater, but less than 0.05%.

[0016] <u>Zn</u>

Zn is an element that is added as needed because it acts to improve the resistance to solder peeling. The desired effect of this action is not realized when the Zn content is less than 0.05%, while if the Zn content exceeds 2.0%, the electrical conductivity and stress relaxation properties will deteriorate. Therefore, the Zn content was set at 0.05 to 2.0%.

[0017] Sn, In, Mn, P, and Si

These elements primarily act to improve the strength by forming a solid solution without greatly reducing the electrical conductivity of the alloy. Consequently, one or more of these elements is added as needed. However, the desired effect of this action will not be obtained if the total amount added is less than 0.01%, while if the total amount added exceeds 1.0%, there will obvious deterioration of electrical conductivity and workability of the alloy. Therefore, the total amount of Sn, In, Mn, P and Si contained in the alloy was set at 0.01 to 1.0%, both for the case where one is added alone and the case where two or more are added in combination with one another.

[0018] B) Crystal grain size (average crystal grain size)

The average crystal grain size of the alloy was limited to 35 to 100 µm taking into consideration bendability and stress relaxation properties. In general, a smaller crystal grain size is preferred in terms of bendability, but a larger crystal grain size is preferred in terms of stress relaxation properties. Nevertheless, the copper alloy having the structure relating to the present invention simultaneously manifests excellent bendability and

excellent stress relaxation properties when the crystal grain size is adjusted to within a range of 35 to 100 μ m relative to the average crystal grain diameter. That is, if the average crystal grain size is less than 35 μ m, bendability will improve further, but stress relaxation will tend to occur, while if the average crystal grain size exceeds 100 μ m, stress relaxation will not tend to occur, but bendability will deteriorate and properties for electronic devices will be inferior.

[0019] Furthermore, the crystal grain size of the alloy can be adjusted during solution annealing, and the desired grain size can be obtained by adjusting the treatment temperature, the treatment time, and the like.

[0020] The effect of the present invention will now be described in specific terms with working examples.

[Working Examples] First, using electrolytic copper or oxygen-free copper as the starting material, copper ingots with the composition shown in Table 1 (thickness of 30 mm) were made in an inert ambient atmosphere inside a high-frequency melting furnace. Next, each treatment of hot rolling, solution annealing, and cold rolling were performed in succession on each of the ingots, the product was aged at 400°C, and the aged product was cold rolled and strain annealed to obtain a sheet.

[0021]

[Table 1]

Alloy	Chemical component (wt%)												Crystal
species		Ti	Cr	Zr	Mg	Zn	Sn	In	Mn	P	Si	Cu and	grain
					•		:					impurities	size
						1							(µm)
Alloys of	1	2.3	0.41	0.16	0.010							Remainder	95
the present	2	0.7	0.37	0.19	0.031							Remainder	65
invention	3	0.9	0.28	0.12	0.022							Remainder	70
	4	2.0	0.54	0.28	0.025	0.1						Remainder	45
	5	1.8	0.39	0.14	0.033	0.3			 .			Remainder	60 .
	6	3.1	0.32	0.21	0.028		0.1					Remainder	80
	7	2.7	0.29	0.16	0.042					0.02		Remainder	65
	8.	1.7	0.43	0.30	0.026				0.3			Remainder	75
	9	3.6	0.21	0.15	0.039						0.3	Remainder	90
	10	1.2	0.51	0.22	0.047			0.2				Remainder	58
	11	1.5	0.37	0.15	0.017	1.0					0.1	Remainder	90
	12	0.2	0.60	0.28	0.028	0.8	0.3					Remainder	85
	13	0.6	0.54	0.30	0.030	0.4		0.2				Remainder	55
	14	0.4	0.26	0.11	0.008	0.3			0.1			Remainder	65
	15	0.1	0.30	0.20	0.011	1.8				0.04		Remainder	39
	16	0.5	0.54	0.31	0.021	1.0			0.1	0.03		Remainder	45
	17	1.9	0.42	0.17	0.040	1.1		0.2			0.1	Remainder	50
	18	1.1	0.60	0.25	0.026	0.4	0.2		0.1			Remainder	72
Alloys of	19	0.9	0.70	*0.002	*_							Remainder	*105
the	20	1.5	0.34	0.21	*	0.5						Remainder	*190
Comparative	21	*6.5	*0.88	0.39	0.018	0.3						Remainder	*130
Examples	22	2.0	0.42	0.14	*0.0001							Remainder	*1.5
	23	0.5	0.40	0.24	0.044	0.6					0.2	Remainder	*2
	24	1.8	0.50	0.19	*0.180	*5.1	0.5					Remainder	*1
	25	*0.001	*0.002	*0.71	*0.087	1.1		0.3				Remainder	75
	26	0.8	0.45	0.24	0.037	0.8			0.1	0.05		Remainder	*110

^{*}The asterisk indicates that the conditions are outside those specified by the present invention.

[0022] Moreover, a test piece of each alloy type was obtained from the resulting sheets and material tests were conducted to evaluate their properties as a "lead frame material" and a "spring material." Furthermore, the properties for use as a "lead frame material" and as a "spring material" were evaluated by studying "strength," "elongation," "electrical conductivity (heat release)," "spring properties," "resistance to solder peeling with heat," "bendability," and "stress relaxation properties."

[0023] "Strength" and "elongation" were evaluated by means of tensile tests, and "electrical conductivity" was found by measuring "conductivity" (%IACS). Moreover, "spring properties" were found by measuring the spring critical value (Kb).

[0024] "Resistance to solder peeling with heat" was studied by the method whereby a material is plated with solder (90% Sn-10% Pb) to a thickness of 5 µm, the product is kept for 1,000 hours in a high-temperature chamber at 150°C during which time the product is removed every 100 hours and bent 90° in both directions, and the time when the solder begins to peel is determined. Samples in which there was no peeling after 1,000 hours are represented as "1,000 hr" in the peeling test results.

[0025] "Bendability" was evaluated by performing bending with W bend test samples and macroscopically observing the bend in the sheet for "irregularities in texture" and "cracks." The evaluation results were represented as

O: no texture irregularities or cracks and

X: texture irregularities or cracks.

[0026] "Stress relaxation properties" were evaluated by anchoring one end of a rectangular sheet, applying bending stress to the other end at 150°C for 1,000 hours, and measuring the residual strain when the stress was released. These test results are shown in Table 2.

[0027]

[Table 2]

Alloy species		Tensile strength (N/mm²)	Elongation (%)	Spring critical value (N/mm²)	Electrical conductivity (%IACS)	Solder peeling start time (hr)	Bendability	Stress relaxation properties (% relax- ation)
Alloys of	1	898	5.1	643	20.1	500	0	7
the present	2	765	6.3	512	22.8	500	ō	9
invention	3	749	6.0	557	23.0	500	Ō	8 .
	4	875	6.2	664	17.9	800	ō	9
	5	915	5.5	779	14.8	900	ō	5
	6	945	3.9	756	13.9	500	0	5
	7	887	4.6	621	16.9	500	0	4
	8	926	5.9	786	16.2	500	ō	4
	9	978	3.8	804	13.0	500	0	5
	10	813	5.9	603	15.9	500	0	5
	11	818	6.3	544	15.3	1000	0	6
	12	708	6.9	571	44.9	1000	0	7
	13	782	8.0	573	20.6	1000	0	7
	14	747	7.9	603	26.6	900	0	9
	15	635	8.9	489	68.8	800	0	10
	16	696	6.3	595	26.4	1000	0	9 .
	17	835	4.8	697	19.3	1000	0	7
	18	801	5.7	670	23.6	700	0	8
Alloys of	19	532	7.3	487	26.8	500	X	9
the	20	857	5.5	620	18.6	1000	X	6 .
Comparative	21	1410	4.5	985	8.8	1000	X	8
Examples	22	930	5.7	704	14.2	500	0	16
	23	680	7.7	543	24.5	700	0	15
	24	742	6.2	514	12.6	1000	0	15
	25	530	6.6	428	16.7	1000	0	5
	26	850	5.8	609	17.7	500	X	6

[0028] The following is clear from the results in Table 2. That is, alloys 1 through 18 of the present invention are superior in terms of strength, conductivity, bendability, and stress relaxation properties, and sufficiently good evaluations were obtained for the other properties.

[0029] In contrast to this, the Zr content of Comparative Alloy 19 was insufficient and its strength was therefore inferior, and the Ti content of Comparative Example 21, and the Zn and Mg contents of Comparative Example 24 exceeded the upper limit and

the electrical conductivity was therefore inferior. Moreover, the Ti and Cr contents of Comparative Example 25 were insufficient and the Zr and Mg contents exceeded the upper limits; therefore, its strength and electrical conductivity were very inferior.

[0030] The crystal grain size (average crystal grain size) of Comparative Examples 22, 23, and 24 was below the lower limit; therefore, even though their bendability was good, their stress relaxation properties were inferior. On the other hand, the crystal grain size of Comparative Alloys 19, 20, 21, and 26 was larger than the upper limit; therefore, their bendability was inferior.

[0031]

[Summary of Effects]

As was described above, the present invention has effects that are very useful industrially in that it makes it possible to provide a copper alloy having high strength and high conductivity that has excellent strength, conductivity, bendability, stress relaxation properties, and the like and that is ideal as a lead frame material, a spring material, or other components of electronic equipment; it has a strong impact in improving the properties of electronic devices.